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(56) Documents cited

GB 1537228
GB 1513525
EP 0103309

(58) Field of search

C3R
B2E

(54) Steel article having heavy-duty anticorrosive coating

(57) A heavy-duty anticorrosive coating is formed on a steel article by subjecting all or a part of the surface to a pretreatment and then forming a polyurethane coating thereon which is formed by reacting a mixture comprising as the main components, (a) a polyol having the main chain composed solely of carbon atoms and hydrogen atoms and containing at least two hydroxyl groups in the molecule and (b) an organic polyisocyanate compound, and an optional organic compound capable of reacting with the polysocyanate compound (b). Preferably, the polyurethane-forming mixture is composed of (a) the polyol, (b) the polyisocyanate compound, (c) an optional polyol, other than the polyol (a), having a hydroxyl value not larger than 120 mg KOH/g, (d) an optional compound having at least two hydroxyl groups and/or amino groups in the molecule and having a hydroxyl value or amine value larger than 120 mg/KOH/g, and optional catalyst, extender, plasticizer and/or hygroscopic compound.

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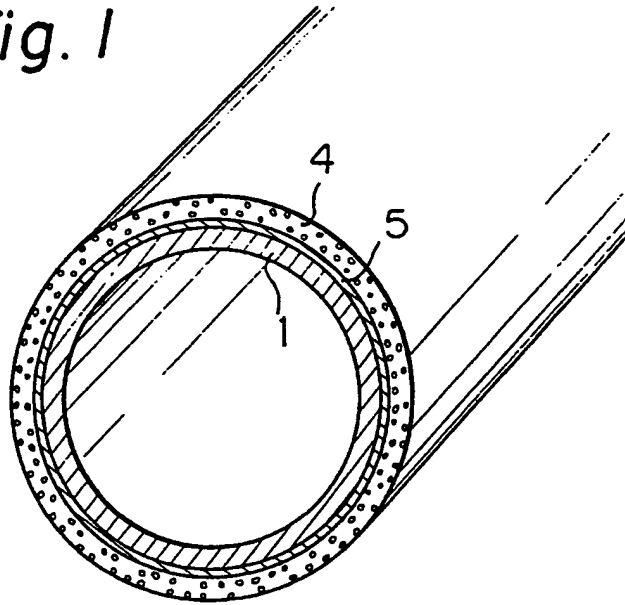
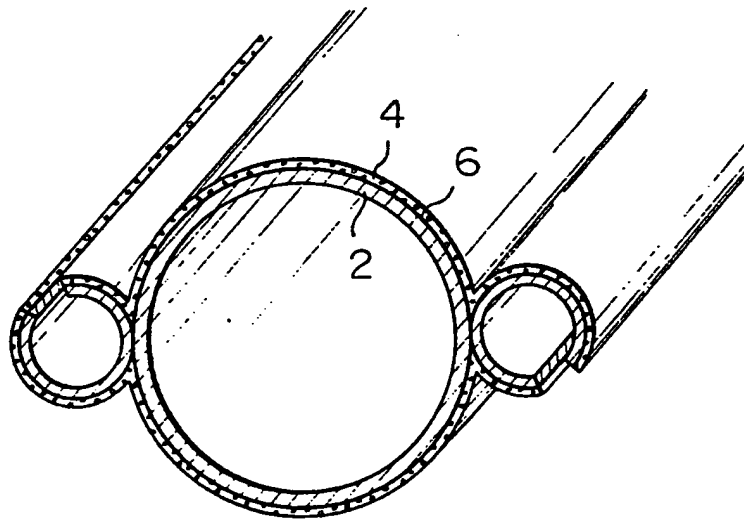
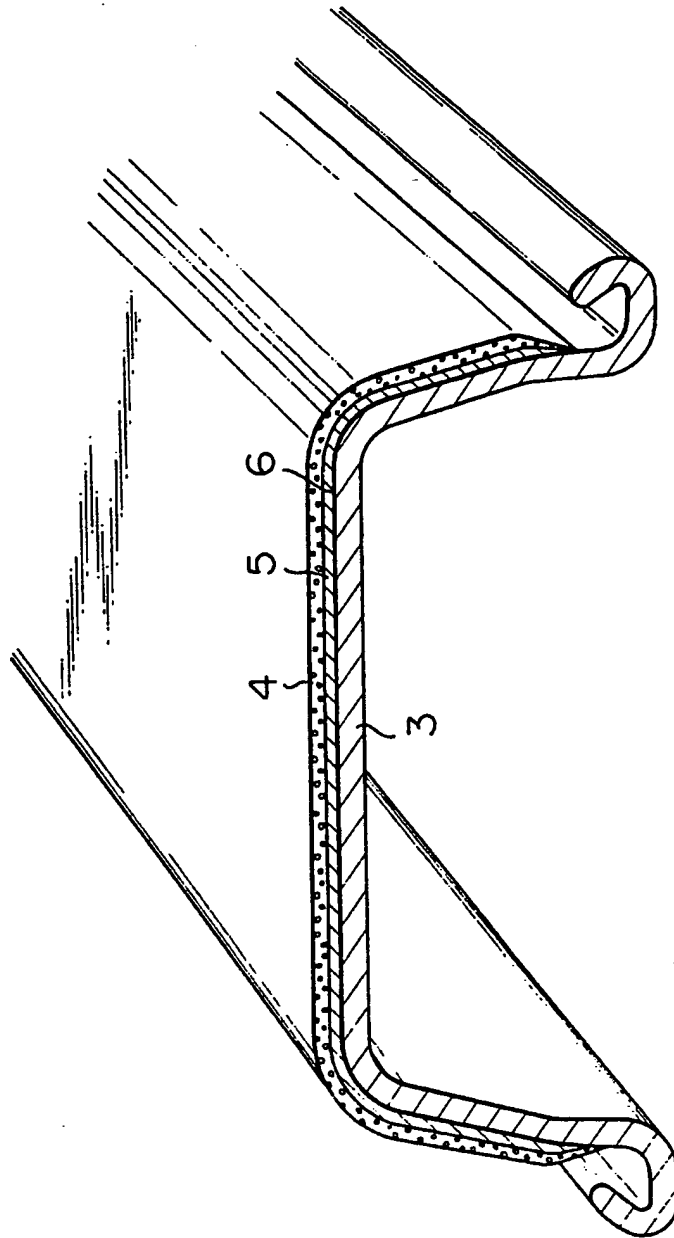
Fig. 1*Fig. 2*

Fig. 3



SPECIFICATION

Steel Article Having Heavy-Duty Anticorrosive Coating

Background of the Invention

(1) Field of the Invention

- 5 The present invention relates to a steel material or article having a novel heavy-duty coating, which is 5
capable of assuredly preventing corrosion and subsequent destruction of a pipe, a vessel, a construction or
the like even when it is used under the ground or in a harbor or river for a long time.

(2) Description of the Related Art

- 10 In the field of steel materials or articles having a heavy-duty anticorrosive coating, wide use was made 10
of steel materials or articles coated with asphalt, fiber-reinforced asphalt or coal tar enamel, and steel
materials coated with a coal tar epoxy resin. Recently, polyethylene-coated steel pipes, which are cheap and
have excellent corrosion resistance (see Japanese Unexamined Patent Publications No. 50-2072, No.
50-143114 and No. 47-34657) have been used for pipes and steel pipes for construction work. As the
heavy-duty anticorrosive coating for steel materials other than steel pipes, there have been proposed a
15 polyurethane mastic coating (Japanese Examined Patent Publication No. 59-20077), an epoxy mastic 15
coating (Japanese Unexamined Patent Publication No. 57-133117) and a glass fiber-reinforced plastic
coating (Japanese Unexamined Patent Publication No. 58-29916).

- Coating materials such as asphalt, fiber-reinforced asphalt and coal tar are defective in that, at high
temperatures, they soften and become difficult to handle, and at low temperatures, they become brittle and
20 are readily cracked. When these coating materials are used for coating, they must be heated to be fused. 20
This coating operation requires a great deal of skill and there arise problems such as the generation of
stimulative gas and smell and the risk of self-ignition.

- Furthermore, coal tar epoxy resin-coated steel materials have problems in that the curing speed of the
coating is low, the operation adaptability after the coating operation is poor and since the strength of the
25 coating is insufficient, deep cracks or penetrations are readily formed in the coating during transportation or 25
working and peeling of the coating or pitting is readily advanced from these cracks or penetrations.
Moreover, a glass fiber-reinforced plastic coating is disadvantageous in that the coating cost is high.

- The polyethylene coating has problems in that the coating equipment is large and cumbersome and a
steel article having a complicated shape such as a steel pipe sheet pipe cannot be coated.
30 Moreover, the polyurethane mastic coating or epoxy mastic coating is unsatisfactory in that since an 30
epoxy resin or a conventional polyurethane resin has hydrophilic groups in the molecule, the coating has a
large water absorbing property and in a corrosive environment, the coating layer absorbs water to cause a
reduction in the electrical insulating characteristics.

Summary of the Invention

- 35 It is therefore a primary object of the present invention to eliminate the defects of conventional steel 35
articles having a heavy-duty anticorrosive coating, namely, to provide a steel article having a heavy-duty
anticorrosive coating, which has excellent corrosion resistance, water resistance, impact resistance and
electrical insulation resistance.

- In accordance with the present invention, there is provided a steel article having a heavy-duty
40 anticorrosive coating, which is obtained by subjecting all or a part of the surface of a steel article to a 40
pretreatment and forming thereon a coating of a polyurethane resin, wherein the polyurethane resin
coating is formed by reacting a mixture comprising, as the main components, (a) a polyol having the main
chain composed solely of carbon atoms and hydrogen atoms, containing at least two hydroxyl groups in
the molecule and preferably having a hydroxyl value not larger than 120 mg KOH/g, and (b) an organic
45 polyisocyanate compound. 45

- According to a preferred embodiment of the present invention, the polyurethane resin comprises (a) a
polyol compound having a hydroxyl value not larger than 120 mg KOH/g, (b) an organic polyisocyanate, an
organic compound, which is reactive with the organic polyisocyanate (b) and is, preferably, (c) a polyol
having a hydroxyl value not larger than 120 mg KOH/g, other than the polyol compound (a), and/or (d) a
50 compound having at least two hydroxyl groups and/or amino groups in the molecule and a hydroxyl value 50
and/or amine value larger than 120 mg KOH/g and, optionally, a catalyst, an extender, a plasticizer and a
hygroscopic compound. The composition of the respective components is such that the amount of the
polyol (a) is (100-x) parts by weight (in which x is from 0 to 50), the amount of the polyol (c) is x parts by
weight (x is as defined above), the amount of the compound (d) is 0 to 300 parts by weight, the amount of
55 the compound (b) is such that the molar ratio $\text{NCO}/(\text{OH} + \text{NH}_2)$ of the isocyanate groups of the compound (b) 55
to the sum of hydroxyl and amino groups of the polyol (a), the polyol (c) and the compound (d) is in the
range of from 0.85 to 1.5, the amount of the catalyst is 0 to 10 parts by weight, the amount of the extender is
0 to 500 parts by weight, the amount of the plasticizer is 0 to 100 parts by weight and the amount of the
hygroscopic compound is 0 to 30 parts by weight.

60 Brief Description of the Drawings 60

Fig. 1 is a perspective view of a steel pipe having a heavy-duty anticorrosive coating, obtained in
Example 1;

Fig. 2 is a perspective view of a steel pipe sheet pile having a heavy-duty anticorrosive coating, obtained in Example 2; and

Fig. 3 is a perspective view showing a steel sheet pile having a high-duty anticorrosive coating, obtained in Example 3.

5 Description of the Preferred Embodiments

The steel article having a heavy-duty anticorrosive coating according to the present invention will now be described in detail.

As the polyol (a) of the polyurethane resin used in the present invention, there can be mentioned a hydroxyl-terminated liquid polybutadiene having at least two hydroxyl groups. In view of the elasticity of the coating, it is preferred that the hydroxyl value of the polyol (a) be not larger than 120 mg KOH/g. Preferred polyols are marketed under the tradenames Poly bd R-45HT, Poly bd R-45 and Poly bd CS-15 (supplied by Idemitsu Petro. Chem. Co.), Nisso PBG-2000 and Nisso PBG-3000 (supplied by Nippon Soda Co.), and Polytale (supplied by Mitsubishi Chem. Ind. Ltd.).

As the compound (b), there can be mentioned tolylene diisocyanate (hereinafter referred to as "TDI"), crude diphenylmethane diisocyanate (hereinafter referred to as "crude MDI"), liquid diphenylmethane diisocyanate (hereinafter referred to as "liquid MDI"), hexamethylene diisocyanate, isophorone diisocyanate, methylene-bis(cyclohexyl isocyanate), xylylene diisocyanate, hydrogenated tolylene diisocyanate and hydrogenated xylylene diisocyanate.

As the polyol (c), there can be mentioned polyoxyalkylene polyols, polytetramethylene ether glycol and polyester polyols, each having a hydroxyl group value not larger than 120 mg KOH/g.

As the compound (d), there can be mentioned compounds having at least two hydroxyl groups, such as ethylene glycol, propylene glycol, butane-diol, neopentyl glycol, hexane-diol, octane-diol, hydroquinone, bisphenol A, trimethylol propane, glycerol, pentaerythritol, triethanol amine and bis(2-hydroxypropyl) aniline, and their alkylene oxide addition products; compounds having at least two amino groups, such as diaminodiphenylmethane, methylene-bis(ortho-chloroaniline) (hereinafter referred to as "MOCA"), phenylene diamine, tolylene diamine, ethylene diamine and piperazine; and compounds having at least two amino and hydroxyl groups, such as monoethanol amine, diethanol amine, aminoethylethanol amine and compounds formed by adding an alkylene oxide to parts of amino groups of the above-mentioned compounds having at least two amino groups. The hydroxyl value and/or the amine value of each of these compounds is larger than 120 mg KOH/g.

The polyurethane resin used for formation of the main coating layer in the present invention may further comprise a catalyst, an extender, a plasticizer, and a hygroscopic compound according to need.

As the catalyst, there can be mentioned organometallic compounds such as dibutyltin dilaurate, stannous octoate, dibutyltin diacetate, lead octylate and lead naphthenate, and amine compounds such as triethylamine and triethylenediamine.

As the extender, there can be mentioned inorganic powders such as calcium carbonate, silicates, mica powder and glass flake.

As the plasticizer, there can be mentioned coal tar, process oil, a liquid petroleum resin, dibutyl phthalate, dioctyl phthalate and chlorinated paraffin.

As the hygroscopic compound, there can be mentioned powdery silica gel and zeolite having a variety of fine pores capable of absorbing water therein, anhydrous calcium chloride and gypsum absorbing water as water of crystallization, and calcium oxide capable of absorbing water by reaction with water.

In the polyurethane resin to be used for formation of the coating in the present invention, the mixing ratio of the polyol (a) and the optional polyol (c) is such that the amount of the polyol (a) is 100 to 50 parts by weight and the amount of the polyols (c) is 0 to 50 parts by weight, with the proviso that the sum of the amounts of the polyols (a) and (c) is 100 parts by weight. If the amount of the polyol (a) is smaller than 50 parts by weight, the water absorption of the resin is undesirably increased and hence, the insulation resistance is reduced. Where a polyester polyol is used as the polyol (c), if the amount of the polyol (a) is smaller than 50 parts by weight, deterioration of the resin by hydrolysis is caused.

The compound (d) may be used in an amount of 0 to 300 parts by weight per 100 parts by weight of the sum of the polyols (a) and (c). It is preferred that the average hydroxyl value of the polyols (a) and (c) and the compound (d) or the sum of the average hydroxyl value and the average amine value be 100 to 300 mg KOH/g. Generally, a reduction of the average hydroxyl value results in a reduction of the mechanical strength. On the other hand, the cold resistance is improved by a reduction of the average hydroxyl value, and conversely, as the hydroxyl value is increased, the mechanical strength is improved but the cold resistance is degraded. If the hydroxyl value is further increased, the resin becomes brittle.

The compound (b) should be used in an amount such that the molar ratio $\text{NCO}/(\text{OH} + \text{NH}_2)$ of the isocyanate groups of the compound (b) to the sum of the hydroxyl and amino groups of the polyols (a) and (c) and the compound (d) is in the range of from 0.85 to 1.5. If this ratio is lower than 0.85, curing is insufficient and the resin becomes viscous. On the other hand, if this ratio is higher than 1.5, the free isocyanate group reacts with water in the air and blistering readily occurs in the coating layer.

It is preferred that the amounts of the catalyst, extender, plasticizer and hygroscopic compound, to be used according to need, be 0 to 10 parts by weight, 0 to 500 parts by weight, 0 to 100 parts by weight and 0 to 30 parts by weight, respectively.

Sometimes the steel article having a heavy-duty anticorrosive coating is cut by a gas burner for alteration of the size, etc. at the piping step or the step of assembling a structure. During this cutting operation, cutting is often rendered difficult because the coating layer composed of a polyurethane resin catches alight. In this case, if a flame retardant such as aluminum hydroxide, antimony trioxide or chlorinated paraffin is added to the polyurethane resin, the cutting operation by a gas burner is facilitated.

Where the coated steel article is used outdoors for a long time, whitening of the surface of the coating composed of the polyurethane resin, that is, so-called "chalking", occurs. Chalking is a phenomenon which occurs only in a very top surface portion of the coating and has no substantial influence on the anticorrosive function of the coating. Where, in view of the appearance characteristics, it is necessary to prevent chalking, this can be done by forming a coating of an acrylic urethane resin on the coating composed of the polyurethane resin. Preferably a product formed by reacting an acrylic polymer with a urethane prepolymer having a terminal isocyanate group is used as the acrylic urethane resin.

As the steel article used in the present invention, there can be mentioned, for example, a steel pipe, a steel pipe sheet pile, a steel sheet pile, an H beam and a steel plate. More specifically, there can be mentioned steel pipes for underground piping, submarine piping and ground piping, and piling steel pipes, steel pipe sheet piles, steel sheet piles and H beams for marine construction, sea and river shore protection construction and other exposed constructions such as bridges. To improve the adhesion between the coating layer composed of the polyurethane resin and the steel material, it is preferred that, after cleaning the surface of the steel material by blast working or the like, (1) an epoxy primer layer be formed, (2) a chemical conversion treatment of the chromic acid type be carried out or (3) a chromic acid type chemical conversion treatment be carried out and an epoxy primer layer be then formed thereon. As the chromic acid type chemical conversion treatment agent, there may be used an aqueous solution of a composite oxide of hexavalent chromium oxide and trivalent chromium oxide obtained by partially reducing hexavalent chromium oxide, and a solution formed by adding to the above aqueous solution glycerol or polyvinyl alcohol as a reduction-promoting substance or silica as a substance capable of improving the adhesion to the coating.

As the epoxy type primer lacquer, there may be used a composition comprising a bisphenol A type epoxy resin as a main component and, incorporated therein, a modified amine curing agent and an inorganic pigment according to need.

To obtain a steel article having a heavy-duty anticorrosive coating according to the present invention, the surface of the steel article is cleaned by blasting or the like and a coating composed of a polyurethane resin is then formed thereon. Before formation of the coating layer of the polyurethane resin, and according to need, an epoxy type primer layer is formed on the surface of the steel article or a chromic acid type chemical conversion treatment is carried out, or after the chromic acid type chemical conversion treatment, an epoxy type primer layer is formed.

For formation of the polyurethane resin coating, the following methods may be adopted.

(1) A method in which a first liquid formed by uniformly mixing the polyols (a) and (c) and the compound (d), optionally with predetermined amounts of the catalyst, extender and plasticizer, and the second liquid of the compound (b) are separately stored, and at the time of application, the first and second liquids are mixed together and coated on the steel article by using a two-liquid mixing type spray coater.

(2) A method in which a first liquid (prepolymer) formed by reacting parts of the polyols (a) and (c) and the compound (d) with all of the compound (b) and a second liquid formed by uniformly mixing together the remaining parts of the polyols (a) and (c) and the compound (d), optionally with the catalyst, extender and plasticizer, are separately stored, and at the time of application, the first and second liquids are mixed together and coated on the steel article by a trowel.

(3) A method in which a liquid composition formed by mixing together the respective components is cast on the steel article from the upper portion thereof by using a multiple-component mixing foaming machine and uniformly coated by a trowel or the like.

In these methods, the curing rate may be controlled according to the amount of the catalyst. It is preferred that a relatively thick coating be carried out so that the thickness of the coating layer is at least 1 mm. If a desired thickness cannot be obtained by performing the coating operation only once, the coating operation may be carried out repeatedly.

If spray coating is carried out under specific conditions, for example, under high humidity conditions, water in the air is absorbed and reacts with the isocyanate to form foam in the coating, which results in a reduction of the strength, water absorption and insulating property of the coating. In this case, the formation of foam in the coating can be prevented if coating is carried out after incorporating a hygroscopic compound into the polyurethane resin.

As apparent from the foregoing description, the coated steel article of the present invention has a heavy-duty anticorrosive coating of a polyurethane resin, which has a low water-absorption, a high electrical insulation property, excellent mechanical characteristics and a long-period stability. Accordingly, the coated steel article of the present invention has an excellent corrosion resistance under the ground, in the sea and for other exposed conditions.

In the polyurethane resin of the present invention, the contents of hydrophilic atomic groups such as ether linkages and ester linkage are much lower than in conventional polyurethane resins, and therefore, the water absorption of the polyurethane resin is small. Moreover, the proportion of non-polar hydrocarbon

- groups in the molecule is large and hence, the electrical insulation property is high. Even if the polyurethane coating is exposed to sea water or fresh water, reduction of the electrical insulation property is very small. Accordingly, the coating layer of the present invention retains an excellent corrosion resistance for a long time. The molecular structure of the polyurethane resin of the present invention comprises very soft portions composed of long-chain hydrocarbon groups and rich in the softness, which are known as "soft segments", and portions composed of aromatic rings and highly crosslinked atomic groups and having a high rigidity, which are known as "hard segments". Accordingly, the polyurethane resin of the present invention is characterized in that it has a combination of a high mechanical strength and a high softness. Therefore, the coating of the present invention has a high durability against shock or bending during transportation or working.
- The polyurethane resin of the present invention is distinguishable over conventional polyurethane resins in that since the content of the ester linkage readily undergoing hydrolysis or the ether linkage readily undergoing ultraviolet ray deterioration or oxidative deterioration in the molecule is very low, the coating layer of the polyurethane resin layer of the present invention has an excellent resistance to ultraviolet ray deterioration, resistance to oxidative deterioration, water resistance and chemical resistance. Therefore, the polyurethane resin of the present invention is suitable for forming an anticorrosive coating for piping work or construction which will be in use for a long time and in which intermediate maintenance is difficult.
- The present invention will now be described in detail by the following examples.
- All of "parts in the examples are by weight.

20 EXAMPLE 1

- The outer surface of a steel pipe for water service, which had a thickness of 12 mm, an outer diameter of 1600 mm and a length of 12 m, was cleaned by grit blasting (G-70), and an epoxy type primer was then spray-coated on the cleaned outer surface to form a primer layer having a thickness of 30 μ m (after curing). A polyurethane coating material comprising the first and second components shown in Table 1 was coated on the primer layer by a two-components mixing type spray coating machine to form a coating of a polyurethane resin having a thickness of 2.5 mm (after curing). Fig. 1 is a perspective view of the thus-obtained coated steel pipe having a heavy-duty anticorrosive coating. In Fig. 1, reference numerals 1, 4 and 5 represent the steel pipe, the coating composed of the polyurethane resin and the epoxy type primer layer, respectively.
- The heavy-duty anticorrosive coating of this coated steel pipe was aged for 7 days after the coating operation to sufficiently advance the curing of the coating layer. Test pieces were cut out and subjected to various performance tests. The results obtained are shown in Table 2.

TABLE 1

35	Components	Coating Material Kinds	Amounts (Parts)	35
	First Component			
	Polyol (a)	Polybutadiene R-45HT ¹⁾	100	
	Polyol (c)	—	—	
	Compound (d)	Polyhardener PA-400 ²⁾	65	
40	Catalyst	Dibutyltin dilaurate	0.8	40
	Extender	Mica powder	15	
	Plasticizer	Process oil	45	
	Hygroscopic compound	Anhydrous gypsum	4	
45	Second Component			45
	Compound (b)	Crude MDI	80	

Note

¹⁾Product of ARCO Co. having a hydroxyl value of 46.5 mg KOH/g.

²⁾Product of Daiichi Kogyo Seiyaku Co. having a hydroxyl value of 420 mg KOH/g.

TABLE 2

Test Item	Test Method	Unit	Test Results
Hardness of coating	ASTM D-2240	(Shore D)	63
Tensile strength of coating	ASTM D-638	kg/cm ²	125
Elongation of coating	Ditto	%	60
Impact strength	ASTM G14	kg · m	3.3
Bendability ¹⁾	JIS G-3491	—	No change when bent at radius of 38 mm
Water absorption of coating	Immersed in tap water	%	Saturated at 0.8%
Weatherability	Dew cycle weather meter	—	No reduction of tensile elongation of coating after 8000 hours
Electrical insulation resistance	DIN 30670	$\Omega \cdot m^2$	2.1×10^{11}
Immersion in tap water	Entire surface immersed	—	No separation from artificial scratch even after 90 days

Note

¹⁾Steel plate having thickness of 1.5 mm was bonded to the periphery of the steel pipe after coating, the coated steel plate was peeled and the coating properties were the coated steel plate were tested.

¹⁾All of the tests other than weatherability test were conducted at 25°C.

EXAMPLE 2

The outer surface of a steel pipe sheet pipe having a thickness of 15 mm, an outer diameter of 800 mm, a length of 16 m and a shape as shown in Fig. 2 was cleaned by a grit blast treatment (G-70) and subjected to a chromic acid type chemical conversion treatment to form a film of a chromic acid compound having a total chromium deposition amount of 500 mg/m². A polyurethane coating material comprising first and second components shown in Table 3 was coated on the chromic acid compound film by a two-component mixing type spray coating machine to form a coating of a polyurethane resin having a thickness of 2.5 mm after curing. Fig. 2 is a perspective view showing the thus-obtained steel pipe sheet pile having the heavy-duty anticorrosive coating. In Fig. 2, reference numerals 2, 4 and 6 represent the steel pipe sheet pile, the coating layer of the polyurethane resin and the film composed of the chromic acid compound, respectively.

The heavy-duty anticorrosive coating of the coated steel pipe sheet pile was aged for 7 days to sufficiently advance curing of the coating, and test pieces were cut out and subjected to various performance tests. The results obtained are shown in Table 4.

15

TABLE 3

15

Components	Coating Material Kinds	Amounts (Parts)
First Component		
Polyol (a)	Polybutadiene R-45HT	100
Polyol (c)	—	—
Compound (d)	Polyhardener PA-400	70
Catalyst	Dibutyltin dilaurate	0.6
Extender	Talc	15
Plasticizer	Process oil	40
Hygroscopic compound	Synthetic zeolite	4
Second Component Compound (b)	Crude MDI	85

25

25

TABLE 4

Test Item	Test Method	Unit	Test Results
Hardness of coating	ASTM D-2240	(Shore D)	65
Tensile strength of coating	ASTM D-638	kg/cm ²	133
Elongation of coating	Ditto	%	52
Impact strength	ASTM G14	kg · m	3.7
Bendability	JIS G-3491	—	No change of coating when bent at radius of 38 mm
Water absorption of coating	Immersed in 3% aqueous sodium chloride	%	Saturated at 0.5%
Weatherability	Dew cycle weather meter	—	No reduction of tensile elongation even after 8000 hours
Electrical insulation resistance	DIN 30670	$\Omega \cdot m^2$	2.3×10^{11}
Immersion in aqueous sodium chloride	Entire surface immersed in 3% aqueous sodium chloride	—	No separation of coating from artificial scratch after 90 days

EXAMPLE 3

One surface of a steel sheet pile (FSP III type) having a shape shown in Fig. 3 was cleaned by a grit blasting (G-70) and subjected to a chromic acid type chemical conversion treatment to form a film of a chromic acid compound having a total chromium deposition amount of 500 mg/m². Then, an epoxy resin primer was coated on the chromic acid compound film to form a primer layer having a thickness of 30 μm after curing. A polyurethane coating material comprising first and second components shown in Table 5 was coated on the primer layer by using a two-component mixing type spray coating machine to form a coating of a polyurethane resin having a thickness of 2.5 mm after curing. The obtained coated steel sheet pile having the heavy-duty anticorrosive coating is shown in the perspective view of Fig. 3. In Fig. 3, reference numerals 3, 4, 5 and 6 represent the steel sheet pile, the coating composed of the polyurethane resin, the epoxy resin primer layer and the film composed of the chromic acid compound, respectively.

The heavy-duty anticorrosive coating of the coated steel sheet pile was aged for 7 days to sufficiently advance the curing of the coating. The test pieces were cut out and subjected to various performance tests. The results obtained are shown in Table 6.

TABLE 5

Components	Coating Material Kinds	Amounts (Parts)
First Component		
Polyol (a)	Polybutadiene R-45HT	100
Polyol (c)	—	—
Compound (d)	Polyhardener PA-400	75
Catalyst	Dibutyltin dilaurate	0.6
Extender	—	—
Plasticizer	Chlorinated paraffin	40
Hygroscopic compound	Synthetic zeolite	4
Flame retardant	Aluminum hydroxide	55
Second Component		
Compound (b)	Crude MDI	90

TABLE 6

Test Item	Test Method	Unit	Test Results
Hardness of coating	ASTM D-2240	(Shore D)	68
Tensile strength of coating	ASTM D-638	kg/cm ²	127
Elongation of coating	Ditto	%	57
Impact resistance	ASTM G14	kg · m	3.5
Bendability	JIS G-3491	—	No change of coating when bent at radius of 38 mm
Water absorption of coating	Immersed in 3% aqueous sodium chloride	%	Saturated at 0.4%
Weatherability	Dew cycle weather meter	—	No reduction of tensile elongation of coating after 8000 hours
Electrical insulation resistance	DIN 30670	$\Omega \cdot m^2$	2.2×10^{11}
Immersion in aqueous sodium chloride	Entire surface immersed in 3% aqueous sodium chloride	—	No separation from artificial scratch even after 90 days

From the foregoing performance test results of the steel articles having a heavy-duty anticorrosive coating, obtained in the examples, it is seen that each of the heavy-duty anticorrosive coatings according to the present invention had a high impact resistance and a good bendability. Furthermore, even if the coating was immersed in tap water or aqueous sodium chloride, water absorption of the coating layer was saturated below 1% and increase of the water absorption was not observed afterward. In the dew cycle weathermeter test, no reduction of the tensile elongation was observed in any of the coated steel articles having a heavy-duty anticorrosive coating even after the lapse of 8000 hours, and it was found that each of the coated steel articles according to the present invention had a good weatherability. Moreover, the coated steel article having a heavy-duty anticorrosive coating according to the present invention had a much higher electrical insulation resistance than that of conventional polyurethane resin-coated steel articles. Furthermore, from the results of the tap water and aqueous sodium chloride immersion tests, it was found that the heavy-duty anticorrosive coating of the coated steel material of the present invention could maintain a good adhesion for a long time in either tap water or aqueous sodium chloride.

As seen from the results obtained in the examples, it will be readily understood that the steel article having a heavy-duty anticorrosive coating according to the present invention has excellent impact resistance, bendability, water absorption, weatherability, electrical insulation resistance and adhesion, and the coated steel article shows an excellent long-period durability in sea water or fresh water or under the ground or in other exposed conditions.

CLAIMS

1. A steel article having a heavy-duty anticorrosive coating, which is obtained by subjecting all or a part of the surface of a steel article to a pretreatment and forming thereon a coating of a polyurethane resin, wherein the polyurethane resin coating is formed by reacting a mixture comprising, as the main components, (a) a polyol having a main chain composed solely of carbon atoms and hydrogen atoms and containing at least two hydroxyl groups in the molecule and (b) an organic polyisocyanate compound, and an optional organic compound capable of reacting with the polyisocyanate compound (b).
2. A coated steel article as set forth in claim 1, wherein the hydroxyl value of the polyol (a) is not larger than 120 mg KOH/g.
3. A coated steel article as set forth in claim 1, wherein said organic compound capable of reacting with the organic polyisocyanate compound (b) is selected from the group consisting of (c) polyols other than the polyol (a), having a hydroxyl value not larger than 120 mg KOH/g, and (d) compounds having at least two groups selected from the group consisting of hydroxyl groups and amino groups in the molecule and having a hydroxyl value or amine value larger than 120 mg KOH/g.
4. A coated steel article as set forth in claim 1, wherein said mixture further comprises an optional catalyst, an optional extender, an optional plasticizer and an optional hygroscopic compound.
5. A coated steel article as set forth in claim 4, wherein the composition of the respective components is such that the amount of the polyol (a) is (100-x) parts by weight (in which x is from 0 to 50), the amount of the polyol (c) is x parts by weight (in which x is as defined above), the amount of the compound (d) is 0 to 300 parts by weight, the amount of the polyisocyanate compound (b) is such that the molar ratio $\text{NCO}/(\text{OH} + \text{NH}_2)$ of the isocyanate groups to the total of the hydroxyl and amino groups of the polyol (a), the polyol (c) and the compound (d) is in the range of from 0.85 to 1.5, the amount of the catalyst is 0 to 10 parts by weight, the amount of the extender is 0 to 500 parts by weight, the amount of the plasticizer is 0 to 100 parts by weight and the amount of the hygroscopic compound is 0 to 30 parts by weight.
6. A coated steel article as set forth in claim 5, wherein the catalyst is an organic metal compound selected from the group consisting of dibutyltin dilaurate, stannous octoate, dibutyltin diacetate, lead octylate and lead naphthenate or an amine compound selected from the group consisting of triethylamine and triethylenediamine.
7. A coated steel article as set forth in claim 5, wherein the extender is an inorganic powder selected from the group consisting of calcium carbonate, a silicate, mica and glass flake.
8. A coated steel article as set forth in claim 5, wherein the plasticizer is selected from the group consisting of coal tar, process oil, a liquid petroleum resin, dibutyl phthalate, dioctyl phthalate and chlorinated paraffin.
9. A coated steel article as set forth in claim 5, wherein the hygroscopic compound is selected from the group consisting of powdery silica gel, zeolite, anhydrous calcium chloride, gypsum and calcium oxide.
10. A coated steel article as set forth in claim 1, wherein the pretreatment comprises cleaning the surface of the steel article by blasting and forming thereon an epoxy resin primer layer.
11. A coated steel article as set forth in claim 1, wherein the pretreatment comprises cleaning the surface of the steel article by blasting and subjecting the cleaned surface to a chromic acid type chemical conversion treatment.
12. A coated steel article as set forth in claim 1, wherein the pretreatment comprises cleaning the

surface of the steel article by blasting, subjecting the cleaned surface to a chromic acid type chemical conversion treatment and forming thereon an epoxy resin primer layer.

13. A coated steel article as set forth in claim 1, wherein the steel article is a steel pipe, a steel pipe sheet pile, a steel sheet pile, an H beam or a steel plate.

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